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Reaction effect on the properties of poly(ethylene terephthalate) and poly(styrene-*co*-maleic anhydride) blends

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Abstract

Poly(ethylene terephthalate) (PET) was blended with polystyrene (PS) and poly(styrene-*co*-maleic anhydride) (PScMA). The two blend systems were immiscible based on the glass transition temperatures measured by differential scanning calorimetry (DSC). In the case of 70 and 90% PScMA blends, the reaction between ester groups of PET and maleic anhydride (MAH) sites on PScMA occurred during melt mixing at 280°C for 30 min. The reaction was confirmed indirectly by thermal data, from the increase in the complex viscosity and from the solubility difference between the blends. The particle size in PET/PScMA reactive blends was smaller than that of the non-reactive blends. The mechanical properties such as tensile strength and modulus were not affected by the reaction. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); Poly(styrene-*co*-maleic anhydride); Reactive blend

1. Introduction

There have been many studies on reactive processing of immiscible polymer blends. Reactive processing involves in situ reactions of functionalized components to form *block* or *graft* copolymers at the interface between the phases [1–10].It is well known that maleic anhydride (MAH) reacts with polyolefin [11,12] in the presence of radical reagents when mixed at the molten state. Hence, MAH has been used as a compatibilizer in immiscible polymer blends. Especially the blends containing polyamide (PA) have been studied due to the reaction of the amino-chain end of PA and MAH sites on the second component having MAH.

There are a few studies on the reactive processing between poly(ethylene terephthalate) (PET) and maleated polymers. Sambaru and Jabarin [13] have studied PET/HDPE blends using MAH as a compatibilizer. Stretching the blends resulted in fibrillar morphology and improvement in directional mechanical properties. In our previous paper [14], PP/PET and maleic anhydride-grafted PP (MAgPP)/PET systems were undertaken. We confirmed the reaction of ester groups of PET and MAH sites on MAgPP during melt mixing, resulting in the improvement of the dispersibility and higher modulus in MAgPP/PET reactive blends when compared to PP/PET blends.

In this work, we tried to compare the properties of PET/polystyrene (PS) physical blends (without MAH) and PET/poly(styrene-*co*-maleic anhydride) (PScMA) reactive ones (with MAH). Thermal, mechanical and rheological properties as well as the morphology of physical and reactive blends were measured.

2. Experimental

2.1. Materials

The materials used in this study were PS (Aldrich Chemical; $M_w = 273,500$, $T_g = 104°C$) and PScMA (Aldrich Chemical; $M_w = 236,000$, $T_g = 122°C$). MAH content in PScMA was 7 wt%. PET was supplied by Tongkook Synthetic Fibers Co. Ltd, and its weight average molecular weight (M_w) was 38,800. The average molecular weight before and after heat treatment at 280°C for 30 min, the melting, and the glass transition temperatures of the polymers are listed in Table 1.

2.2. Blend preparation

Physical and reactive blends were prepared in a polymerization reactor [15] with agitator (small batch scale) at

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Table 1
Properties of polymers used in this work

Materials	M_w	M_n	T_g (°C)	T_m (°C)	T_c[a] (°C)
PS	273,500 (243,000)[b]	102,500 (76,000)	104	–	–
PScMA[c]	236,000 (226,000)	85,000 (75,000)	122	–	–
PET	38,000 (32,000)	19,400 (16,000)	80	258	150

[a] Crstallization peak temperature at a heating rate of 20°C/min.
[b] Values measured by GPC after heat treatment at 280°C for 30 min.
[c] Maleic anhydride (MAH) content was 7 wt%.

280°C for 30 min. Pure PS, PScMA and PET were treated to have the same thermal history for comparison.

2.3. Measurements

The molecular weights of polymers before and after melt mixing at 280°C for 30 min were measured by gel permeation chromatography (GPC) (JASCO, 807-IT). All samples are dissolved in tetrahydrofuran (THF) at a constant concentration 0.1 wt%. Thermal analysis was performed using a differential scanning calorimetry (DSC) (DuPont 910) under a nitrogen atmosphere. Samples were melted at 280°C for 5 min, and then quenched into liquid nitrogen. The quenched samples were heated from −50 to 300°C at a heating rate of 20°C/min. The tensile properties such as the initial modulus measured at 0.2% elongation, the tensile strength at yield were measured using an Instron Model 4467 universal instrument. Measurements were made at room temperature at a constant crosshead speed of 2 mm/min on specimens slowly cooled after moulding by Mini Max Molder (CS-183MMV-203). The data were taken as averages of at least five measurements. Morphology of the blends was measured by scanning electron microscopy (SEM) (Hitachi, S-2400SEM). Rheological properties such as storage modulus, G' and loss modulus, G'', and complex viscosity, η^* were measured with frequency at 280°C by Physica, Rheo Lab. MC 120.

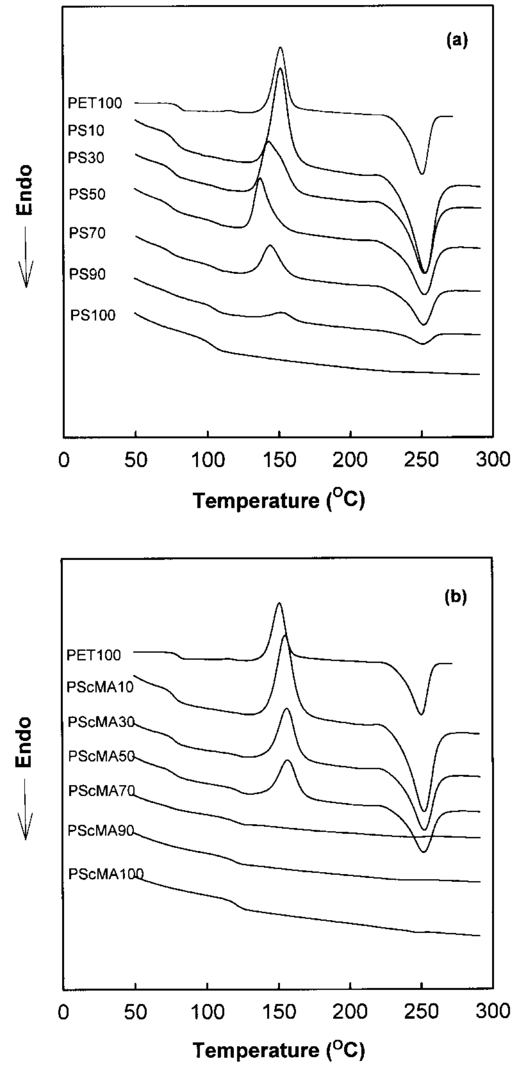

Fig. 1. DSC curves for: (a) PET/PS blends; (b) PET/PScMA reactive blends.

3. Results and discussion

3.1. Thermal analysis

Since the blends were prepared at 280°C for 30 min, the degradation of the constituent polymers are to be checked. Table 1 shows the molecular weights of pure PET, PS and PScMA before and after thermal treatment at 280°C for 30 min. Their molecular weights were decreased after thermal treatment.

Fig. 1 shows DSC curves of PET/PS physical blends and PET/PScMA reactive ones. Both of them show the two glass transition temperatures, which do not change with the blend composition. Hence two blends are immiscible based on the glass transition temperatures. The melting temperatures of PET in two blend systems are seen to remain independent of blend composition, with no depression of melting temperature. In PET/PS physical blends, the melting temperatures of PET were observed in the whole blend compositions, whereas, in PET/PScMA reactive blends, it was not detected above 70% PScMA. The peak crystallization temperature of PET in PET/PS physical blends decreases up to 50% PS, and thereafter increases.

In a number of investigations [16–22], blending of PET

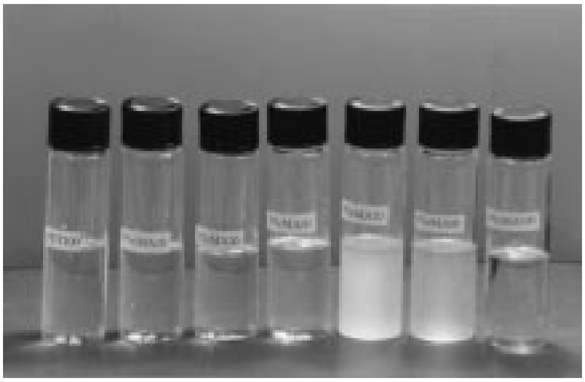

Fig. 2. Solubility test for PET/PScMA blends dissolved in THF.

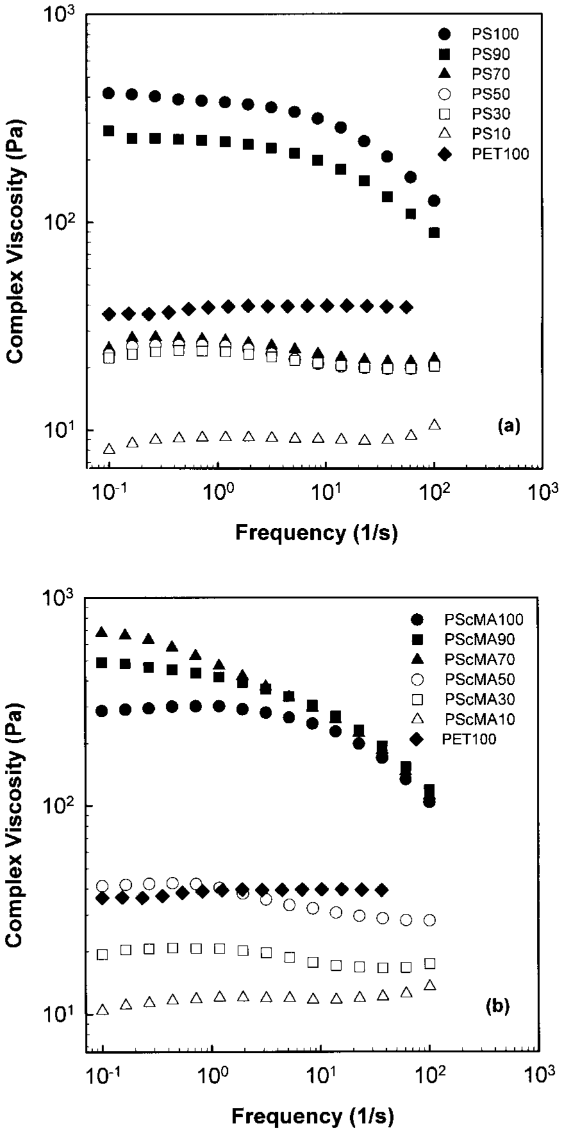

Fig. 3. Complex viscosities with frequency for: (a) PET/PS blends; and (b) PET/PScMA reactive blends at 280°C.

with amorphous polymers such as polycarbonate (PC), polyestercarbonate (PEC), and polyarylate (PAr), was found to result in the reduction of the crystallization of PET. All these amorphous polymers exhibit glass transitions higher than that of PET and they form partially or completely miscible blends with PET. Thus, a drop in the crystallization rate was attributed to the increase in the glass transition leading to a narrower temperature range of crystallization for PET.

In case of immiscible blends containing a second noncrystallizing polymer, the effect of the second phase on the overall rate of crystallization was found to be either positive or negative depending on the conditions of crystallization, composition, molecular structure and molecular weight of the noncrystallizing component. It was reported that the blends of PET with amorphous polymers such as polymethylmethacrylate (PMMA) [23] and aromatic polyamide [24] increased the PET crystallization rate.

It is believed that the increase in the crystallization rate of PET in PET/PS physical blend results from the effect of the small molecules, the degradation product of PS. The important difference between the two blend systems in Fig. 1 is that the crystallization and melting peaks in PET/PScMA reactive blends were not observed at the compositions of more than 50% PET. It may due to the reaction between PET and PScMA. In order to confirm the reaction, solvent extractions were tried in regard to the polymer blend under various blending ratios. Fig. 2 shows the solubility of the blends dissolved in tetrahydrofuran (THF). PScMA was completely dissolved in THF, whereas PET was undissolved and shown at the bottom. The blends having more than 50% PET showed clear solutions and undissolved PET was at the bottom. However, 70 and 90% PScMA blends showed turbid solutions. It indicates that the reaction between PET and PScMA occurred, and the reaction product was not dissolved completely in THF. To measure the extent of reaction, we tried to use the spectroscopic methods such as UV and ^{1}H NMR, but it was not possible.

3.2. Rheological properties and morphology

It has been demonstrated that, when dealing with a immiscible polymer blend, the morphology of the blend controls its rheological properties. Hence we will discuss the rheological properties and the morphology together in order to investigate the difference between PET/PS and PET/PScMA blends.

Fig. 3(a) shows the complex viscosity of PET/PS physical blends. The linear relationship between the blend compositions and viscosity was not observed. Especially the blends having more than 30% PET produce viscosity lower than that of pure PET even though PS viscosity is significantly higher. It indicates that PET/PS blend is immiscible, and forms two phases, giving rise to discrete–continuous phase morphology, as may be seen in Fig. 4. Note that in Fig. 4 PS forms the discrete (i.e. droplets)

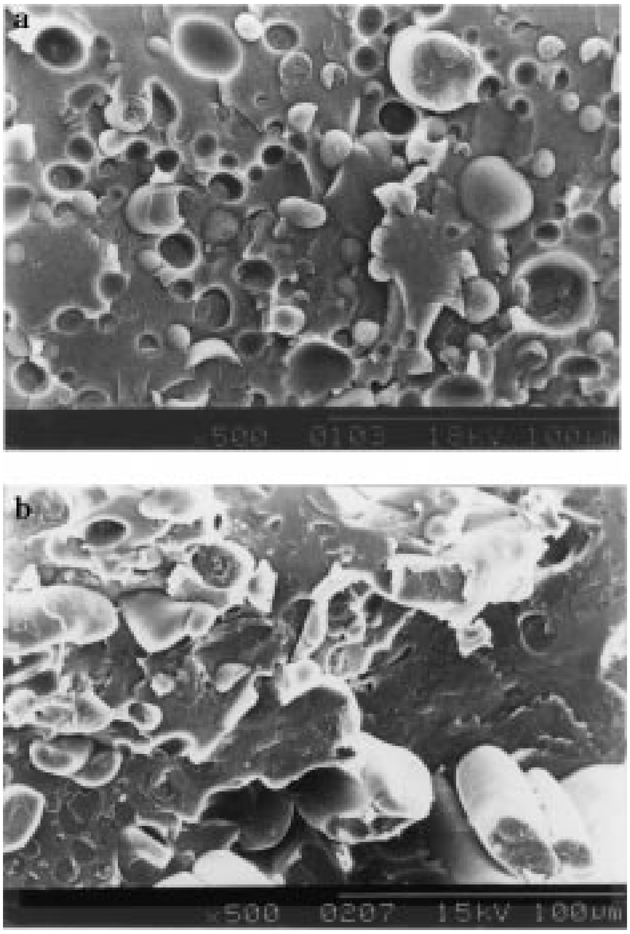

Fig. 4. SEM photographs of: (a) PET/PS (70/30); and (b) PET/PS (30/70) blends.

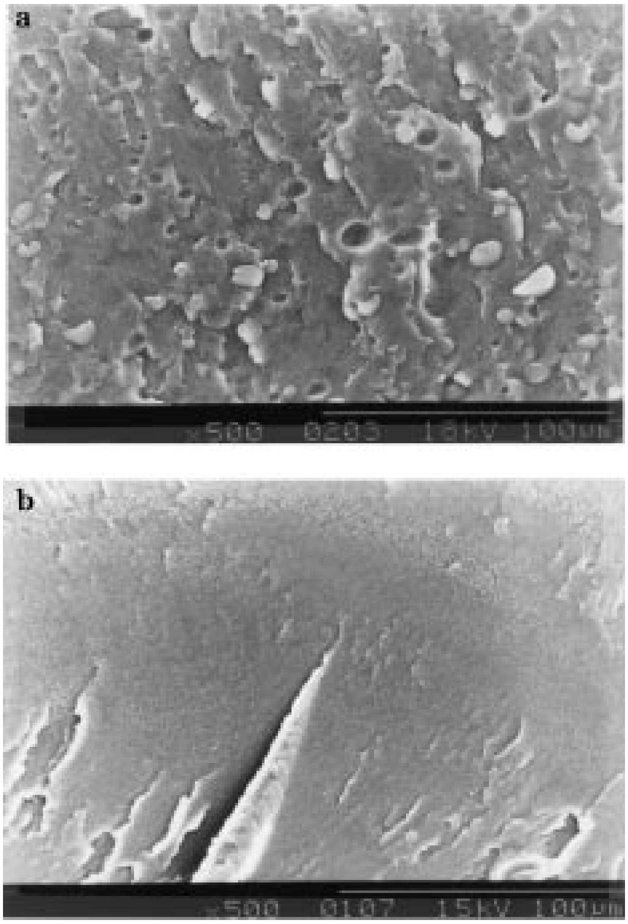

Fig. 5. SEM photographs of: (a) PET/PScMA (70/30); and (b) PET/PScMA (30/70) blends.

dispersed in the continuous PET phase for the PET/PS 70/30 blend, and PET forms the discrete phase dispersed in the continuous PS phase for the PET/PS 30/70 blend. Fig. 4(a) shows that PS droplets have a well-defined spherical shape. The droplet surface and surface of holes left by the PS spheres appears to be very smooth. In addition, during the fracture process, a large number of droplets were pulled out from their previous position. This observation suggests poor adhesion between the PS phase and PET matrix. On the contrary, PET droplets as shown in Fig. 4(b) do not have a well-defined spherical shape. It is thought that it may result from the difference of the viscosity of matrix.

Fig. 3(b) shows the complex viscosity of the PET/PScMA reactive blends. It also indicates that the viscosity of the blends does not depend on the blend compositions, and the viscosities of the PET-rich compositions are lower than that of pure PET. Interesting is the viscosity of 70 and 90% PScMA blends which has a higher value than that of the pure PScMA. As mentioned earlier, these two blend compositions dissolved in THF showed turbid solution compared to the other blend solutions. It was thought that the reaction between PET and PScMA occurred, as a result of which, the ester groups of PET reacted with the maleic site of PScMA, forming the graft polymer. This therefore, results in an increase in the viscosity. This result can be understood through the morphology as shown in Fig. 5. Fig. 5(a) shows the PScMA

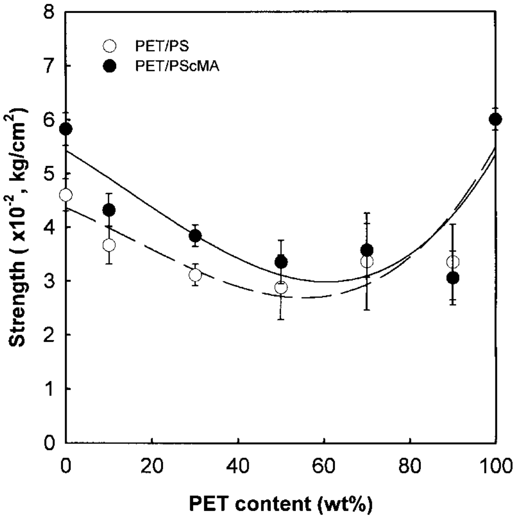

Fig. 6. The tensile strength of PET/PS physical blends (○) and PET/PScMA reactive blends (●) with the content of PET at yield.

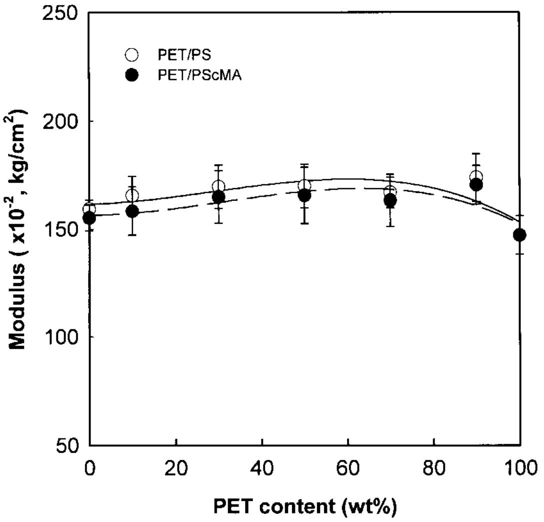

Fig. 7. The initial modulus of PET/PS physical blends (○) and PET/PScMA reactive blends (●) measured at 0.2% elongation with the content of PET.

droplets dispersed in the continuous PET phase for the PET/PScMA 70/30 blend. Compared with the physical blend as shown in Fig. 4(a), the droplet size was decreased and its size distribution is narrower than that of the physical blend. It suggests that the interaction between PET and PScMA is present even though it cannot affect the miscibility. On the contrary, the PET droplet in PET/PScMA 30/70 blend was not observed in Fig. 5(b), and the blend seems to be miscible. This apparent homogeneity could be caused by the small particles not observed by SEM.

3.3. Mechanical properties

Fig. 6 shows the tensile strength at the yield of physical blends and reactive ones. In both systems, the tensile strengths were lower than the additive values of component polymers. Probably, the reaction effect was not big enough to provide a good adhesion between the two phases.

Fig. 7 shows the tensile modulus at 0.2% elongation of physical blends and reactive ones. The difference in modulus between the two blend systems was not detected. In both systems, the modulus of the blends did not change with the content of PET.

Thus, the effect of reaction in 70 and 90% PScMA blends was not observed in mechanical properties.

4. Conclusions

The reactive blend of PET and PScMA was prepared and compared with the properties of PET/PS physical blend. We expected that the reaction between ester groups in PET and maleic sites in PScMA would affect the properties of the blends. The reaction was observed in 70 and 90% PScMA blends. It was confirmed indirectly from the solubility of the blends in THF. The reaction between the ester groups in PET and MAH sites in PScMA produces a graft polymer, which increases the viscosity of the blends. Besides these two blend compositions, morphology indicates that there are interactions between two phases in all PET/PScMA blend compositions. However, the interaction was not enough to affect the thermal and rheological properties except for 70 and 90% PScMA blends. The reaction effect on the mechanical properties was not observed even though it occurred.

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